A Uniform Basis for Reporting Analytical Data on Fatty Materials[1]

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THE CHEMISTRY of the fatty acids and their derivatives is one of the oldest branches of organic chemistry, dating from Chevreul. The development of the field required some means of measuring purity and identity of pure compounds and of analyzing complex natural and industrial mixtures. The gradual evolution led to a variety of methods for analysis of the type and quantity of functional groups. In so doing, certain arbitrary units for these measurements were introduced and their use was perpetuated. Thus there are in existence the iodine number, saponification number, acetyl value, acid number, and so on (1). There is no doubt of their usefulness, but the existence of a variety of definitions and of the arbitrary units (grams of I_2/100 grams of sample, milligrams of KOH/gram of sample . . .) makes intercomparison difficult and their use a needless burden to the memory. In short, their use is a measure of historical impotence. Even the use of percentage itself introduces uncertainty. Thus the use of the term percentage of hydroxyl should mean the percentage by weight of the hydroxyl group and not the weight of oxygen of the hydroxyl group; however both uses appear in the literature.

In all the chemical analytical procedures used there are only two experimental quantities, moles of reagent consumed and the weight of sample. This suggests that a more proper unit of measure would be moles of reagent/gram of sample. Following this, it is suggested that a number, expressed in millimoles per gram, be introduced which is the reciprocal of the molecular weight and that it be called the specific molecular constant $\overline{N}$. Since the specific molecular constant $(\overline{N})$ equals the reciprocal of the molecular weight, its calculation is trivial, and no arbitrary definition or conventional numbers need be memorized. The specific molecular constant $(\overline{N})$ will range from around two to around 20 and is inversely proportional to the molecular weight. The word specific is introduced to indicate per gram as is done in thermodynamics, (e.g., specific heat capacity, specific volume . . .) and the bar over N follows thermodynamic practice for designating specific. The specific molecular constant $(\overline{N})$ is expressed in millimoles per gram for convenience in handling and interpreting data and for ease of remembering.

The results of the various analytical procedures would be reported as specific numbers (m moles/g.). Thus, by following this nomenclature, the specific iodine number $(\overline{N}_I)$, specific saponification number $(\overline{N}_S)$, specific hydroxyl number $(\overline{N}_{OH})$, specific acid number $(\overline{N}_A)$, etc., would replace the usual conventional numbers. All the specific numbers for a pure polyfunctional compound become identical when only one functional group of each type is present. Fur-

ther, if more than one of a particular functional group is present, then its specific number will be an integral multiple of the specific molecular constant.

The equations for obtaining the specific numbers are given below, along with formulas for converting the conventional numbers:

$\overline{N}_x$ = specific number in millimoles of reagent per gram of sample

N_x = conventional number

w = weight of sample in grams

n = normality of reagent used for functional group in equivalents per liter

Δv = volume of reagent for functional group in milliliters corrected for any blank

Equations

Specific iodine number (2)

$$\overline{N}_I = \frac{1/2 \, n \, \Delta v}{w} = \frac{N_I}{25.4}$$

Specific saponification number (3)

$$\overline{N}_S = \frac{n \, \Delta v}{w} = \frac{N_S}{56.1}$$

Specific acid number (4)

$$\overline{N}_A = \frac{n \, \Delta v}{w} = \frac{N_A}{56.1}$$

Specific hydrogen number (5)

$$\overline{N}_H = \frac{v^o}{22.4 \, w} = \frac{10^3}{N_H}$$

(v^o is volume of hydrogen absorbed, corrected to STP)

Specific hydroxyl number (6, 7)

$$\overline{N}_{OH} = \frac{n \, \Delta v}{w} = \frac{N_{OH}}{56.1}$$

(conversion of hydroxyl value)

$$\overline{N}_{OH} = \frac{n \, \Delta v}{w} = \frac{N_{OH}}{1.7}$$

(conversion of percentage of hydroxyl)

Specific acetyl number (6)

$$\overline{N}_{Ac} = \frac{n \, \Delta v}{w} = \frac{N_{Ac}}{56.1}$$

Specific peroxide number (8)

$$\overline{N}_{oo} = \frac{n \, \Delta v}{w} = \frac{N_{oo}}{1.60}$$

Specific carbonyl oxygen (9)

$$\overline{N}_{co} = \frac{n \, \Delta v}{w} = \frac{N_{co}}{1.60}$$

Specific oxirane oxygen (10)

$$\overline{N}_o = \frac{n \, \Delta v}{w} = \frac{N_o}{1.60}$$

Representative specific molecular constants and the corresponding conventional numbers for a variety of pure compounds are tabulated in Table I. The utility of the specific molecular constant is seen for ricinoleic acid where there are three conventional numbers

TABLE I

Compound	Specific molecular constant	Specific numbers (millimoles per gram)					Conventional numbers					
	$\overline{N}$	$\overline{N}_I$	$\overline{N}_S$	N_A	$\overline{N}_{OH}$	$\overline{N}_H$	N_I	N_S	N_A	N^a_{OH}	N_H	N^c_{OH}
Acetic acid	16.65	0	16.65	16.65	0	0	0	934	934	0	∞	0
Stearic acid	3.52	0	3.52	3.52	0	0	0	197	197	0	∞	0
Monohydroxystearic acid	3.33	0	3.33	3.33	3.33	0	0	187	187	5.66	∞	187
Dihydroxystearic acid	3.16	0	3.16	3.16	6.32	0	0	177	177	10.75	∞	355
Ricinoleic acid	3.35	3.35	3.35	3.35	3.35	3.35	85.1	188	188	5.70	299	188
Oleic acid	3.54	3.54	3.54	3.54	0	3.54	89.9	199	199	0	282	0
Linoleic acid	3.57	7.13	3.57	3.57	0	7.13	181	200	200	0	140	0
Linolenic acid	3.59	10.78	3.59	3.59	0	10.78	274	201	201	0	92.8	0
Oleyl alcohol	3.73	3.73	0	0	3.73	3.73	94.5	0	0	6.33	268	209
Linoleyl alcohol	3.75	7.50	0	0	3.75	7.50	191	0	0	6.38	133	210
Epoxystearic acid	3.35	0	3.35	3.35	0	3.35^b	0	188	188	0	299	0
Epoxyoctadecanol	3.51	0	0	0	3.51	3.51^b	0	0	0	5.98	285	197
Methyl butyrate	9.79	0	9.79	0	0	0	0	549	0	0	∞	0
stearate	3.35	0	3.35	0	0	0	0	188	0	0	∞	0
oleate	3.37	3.37	3.37	0	0	3.37	85.6	189	0	0	295	0
linoleate	3.40	6.79	3.40	0	0	6.79	172	191	0	0	147	0
linolenate	3.42	10.26	3.42	0	0	10.26	261	192	0	0	97.5	0
arachidonate	3.14	12.56	3.14	0	0	12.56	319	176	0	0	79.6	0
epoxystearate	3.20	0	3.20	0	0	3.20^b	0	180	0	0	313	0
Mono olein	2.81	2.81	2.81	0	5.62	2.81	71.4	158	0	9.54	356	315

^{a} % Hydroxyl. ^{b} Reduction of epoxy function. ^{c} Hydroxyl value.

($N_I = 85.1$, $N_{OH} = 188$, $N_A = 188$) while the specific numbers equal the specific molecular constant ($\overline{N} = \overline{N}_I = \overline{N}_{OH} = \overline{N}_A = 3.35$). As is seen in Table I for oleic acid, linoleic acid, and linolenic acid, the specific iodine number ($\overline{N}_I$) is in the ratio of 1, 2, and 3, respectively, to the corresponding specific molecular constant ($\overline{N}$) for each compound.

When a complex mixture is being examined, the use of specific numbers will permit a more rapid interpretation and indicate in a more direct fashion the nature of the mixture. This is particularly true when the data are used in conjunction with modern instrumentation, infrared and ultraviolet spectrophotometers, vapor phase chromatography, etc.

Several examples of convenience of the new procedures with mixtures are given below:

Example I

Mixture of alcohol and acid:

Conventional numbers

Iodine number (N_I) = 63.2
Hydroxyl value (N_{OH}) = 83.6
Acid number (N_A) = 118

Specific numbers (millimoles per gram)

Specific iodine number ($\overline{N}_I$) = 1.49
Specific hydroxyl number ($\overline{N}_{OH}$) = 1.49
Specific acid number ($\overline{N}_A$) = 2.11

The identity of the specific iodine and hydroxyl numbers suggests the possibility that the unsaturated and the hydroxyl functions may be in the same molecule and that the acid is saturated. This information is readily available and not buried, as in the conventional numbers.

Example II (hypothetical case)

Unknown triglyceride	$\xrightarrow[\text{treatment}]{\text{enzyme}}$	β-mono-glyceride	+	mixture of acids
Conventional numbers				
N_I 59.2		71.3		47.2
N_S 196		157		209
N_A 0		0		209
Specific numbers (millimoles per gram)				
$\overline{N}_I$ 2.33		2.81		1.86
$\overline{N}_S$ 3.49		2.81		3.71
$\overline{N}_A$ 0		0		3.71

The ratio of the $\overline{N}_S$ to $\overline{N}_I$ in the starting material is 3 to 2, indicating that, since this is a triglyceride, there are only 2 double bonds present. The ratio of $\overline{N}_S$ to $\overline{N}_I$ in the monoglyceride is 1, indicating that the beta-acyloxy group has one double bond and further that the molecular weight is $1/\overline{N}_S$ or 356. Since this is a monoglyceride, the acid residue must be monounsaturated C_{18} (monoglyceride − glycerol + water = 356 − 92 + 18 = 282). The ratio of $\overline{N}_A$ to $\overline{N}_I$ in the acid mixture isolated is 2 and, since there were only 2 double bonds in the original triglyceride and one remains in the monoglyceride, the acid mixture has only one double bond. Combining this with the data for the tri- and monoglycerides leads to the conclusion that the acids isolated have a total carbon content of 34. None of this can be found using the conventional numbers without tortuous calculation.

The following points are to be stressed. The definition of the specific molecular constant provides a rational basis for reporting data in terms of the basic units, moles and grams. The specific numbers provide a more rapid and less cumbersome method of correlating data. The multiplicity of conventional numbers is replaced by a constant or an integral multiple of it, easily obtained from the molecular weight only.

It is suggested that, for an interim period, both the conventional numbers and the specific numbers be reported, and then only the specific numbers.

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